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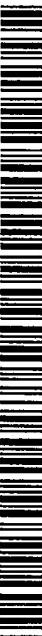
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(54) Title: A WATER-SOLUBLE INJECTION MOULDED CONTAINER

(57) Abstract: A water-soluble, injection-moulded container comprising at least one compartment and having a first opening closed by a first film and a second opening closed by a second film, wherein the first film and the second film have different water dissolution characteristics.

A WATER-SOLUBLE INJECTION MOULDED CONTAINER

The present invention relates to a water-soluble, injection moulded container having at least one compartment and to a
5 process for preparing such a container.

It is known to package chemical compositions, particularly those which may be of a hazardous or irritant nature, in films, particularly water soluble films. Such containers
10 can simply be added to water in order to dissolve or disperse the contents of the container into the water.

For example, WO 89/12587 discloses a package which comprises an envelope of a water soluble material which comprises a
15 flexible wall and a water-soluble heat seal. The package may contain an organic liquid comprising, for example, a pesticide, fungicide, insecticide or herbicide.

WO 92/17382 discloses a package containing an agrochemical
20 comprising a first sheet of non-planar water-soluble or water-dispersible material and a second sheet of water-soluble or water-dispersible material superposed on the first sheet and sealed to it.

25 The above methods of packaging have, however, a number of disadvantages.

The first disadvantage is that they do not have a particularly attractive appearance. In fields such as
30 containers used in the domestic environment, an attractive appearance for an article is extremely desirable. Liquids

contained in envelopes of water-soluble film can have a limp, unattractive appearance.

The second disadvantage is that it is difficult to form two
5 or more separate compartments in the packaging such that two
or more incompatible components are both enclosed but
separated from each other. Although an arrangement has been
described to separate incompatible materials in flexible
pouches in WO 93/08095, the method proposed is complex and
10 is not currently achievable in large-scale manufacturing.
It cannot, therefore, be used for producing large numbers of
containers having at least two compartments. Additionally
it is not possible to ensure that different components are
released at different times or in different environments
15 such as in environments of different temperature or pH.

The third disadvantage is that there is only a limited
control of the release profile of the compositions held in
the containers. For example, when a composition is held
20 between two planar water-soluble films or in a thermoformed
package, the composition is simply released at the time when
the films dissolve or disperse in water. While it may be
possible to control to a certain extent the timing of the
start of release of the contents, there can be no control
25 over the rate of release of the contents since the entire
film dissolves or disperses at about the same time.
Furthermore it can be difficult to provide an extended time
before the contents of the package are released. An
additional problem also arises with thermoformed packages.
30 If the thermoforming is not carefully controlled there may
be inadvertent thinning of the film material at the points
where the film material is drawn down into the mould when it

is thermoformed. This could result in release of the contents of the package early.

The fourth disadvantage is that the containers cannot be
5 produced at a particularly fast rate. When the containers are produced by heat-sealing planar films or by thermoforming, the containers have to be immediately filled and sealed. All of these procedures have to be carried out in succession. This means that it is not possible to obtain
10 a quick throughput for mass-market goods such as household products. For example, standard thermoforming machines can only produce about 400 to 800 containers per minute, and vertical form fill sealing machines can only produce about 120 containers per minute.

15

The present invention seeks to provide a water-soluble container which overcomes some or all of the above disadvantages.

20 The present invention provides a water-soluble, injection-moulded container comprising at least one compartment and having a first opening closed by a first film and a second opening closed by a second film, wherein the first film and the second film have different water dissolution
25 characteristics.

In a preferred feature of the invention we provide a water-soluble, injection-moulded container comprising at least two compartments, a first compartment containing a first
30 composition and having a first opening closed by a first film and a second compartment containing a second composition and having a second opening closed by a second

film, wherein the first film and the second film have different water dissolution characteristics.

The present invention also provides a process for preparing
5 a container as defined above which comprises forming the container comprising at least two compartments by injection-moulding, filling each compartment a composition and sealing each compartment with a film, wherein at least two sealing films have different water dissolution characteristics.

10

The containers of the present invention overcome some or all of the above disadvantages.

Firstly, because the containers are generally rigid and
15 self-supporting, they have an attractive, uniform appearance which does not vary between different containers.

Furthermore, the containers can easily have various elements incorporated which are considered to be pleasing to the eye but which are impossible to incorporate in the flexible
20 containers discussed above.

Secondly, because the containers are generally rigid, it is possible to introduce two or more compartments, or have larger compartments separated by walls, to separate mutually
25 incompatible ingredients. The containers can also hold part of the composition on an external surface, for example in an indentation. Since the films sealing the different compartments of the container have different dissolution characteristics, the contents of the compartments are released at, for example, different times or under different
30 external conditions. Furthermore the container can be

moulded in almost any shape that might be useful. In particular it can be given raised or lowered areas. Thirdly, it is possible to control the release profile of the contents of the container. Since the container is generally rigid it is possible to adapt the thicknesses of some or all of the walls of the container as well as to have sealing films with different water dissolution characteristics to control both the rate of release of the composition as well as the start of release, although the start of release will generally be controlled by the films sealing the compartments.

For example one or more walls may be made thin in order to have an early release of the composition. Alternatively some or all of the walls may be thick in order to ensure that there is a delayed release of the composition. The rate of release of the composition may be controlled by ensuring that only part of the container has thin walls which are dissolved or dispersed before the remainder of the container or by ensuring that the film seals a compartment with a narrow opening which restricts the flow of the contents of the compartment out into the environment. Different walls or parts of walls of the container may be prepared from different water-soluble polymers which have different dissolution characteristics. For example a first component may be fully enclosed by a polymer which dissolves at a higher or lower temperature than the polymer enclosing a second component. Thus different components can be released at different times.

30

In a feature of the invention which comprises a single container with two openings each sealed with a different

film it is to be understood that a formulation is provided in at least part of the container which is only released upon opening of the second film. This can be achieved by use of, for example, a solid or semi-solid formulation that is not 5 released by the opening of the first film.

If the container holds a composition which does not flow, for example a solid or gelled composition, it is not even necessary for the container to fully enclose the 10 composition. A part may be left exposed so that it immediately begins to dissolve when the container is added to water.

Fourthly, since the containers are generally rigid and self-supporting, they can be easily filled on a production line 15 using normal filling equipment. Such equipment is easily capable of filling at least 1,500 containers per minute.

In all embodiments of this invention, the container is, for 20 example, not a container comprising a member, for example, a member formed by injection moulding, having at least two openings positioned on different sides of the member, each opening being closed by a film, which container comprises at least two compartments, each compartment having an opening 25 closed by a film, wherein the film over each opening has different water dissolution characteristics.

Similarly in all embodiments of this invention, the container is, for example, not a container comprising a 30 member having at least two openings positioned on different sides of the member, each opening being closed by a film, each film having different water dissolution characteristics

allowing the container to release different compositions at different temperatures.

Desirably the walls of the container consist essentially of,
5 or consist of, the injection-moulded polymer composition.
It is possible for suitable additives such as plasticisers,
lubricants and colouring agents to be added. Components
which modify the properties of the polymer may also be
added. Plasticisers are generally used in an amount of up
10 to 20 wt%, for example from 15 to 20 wt%. Lubricants are
generally used in an amount of 0.5 to 5 wt%. The polymer is
therefore generally used in an amount of from 75 to 84.5
wt%, based on the total amount of the moulding composition.
Suitable plasticisers are, for example, pentaerythritols
15 such as depentaerythritol, sorbitol, mannitol, glycerine and
glycols such as glycerol, ethylene glycol and polyethylene
glycol. Solids such as talc, stearic acid, magnesium
stearate, silicon dioxide, zinc stearate or colloidal silica
may also be used.

20

It is also possible to include one or more particulate
solids in the moulding composition in order to accelerate
the rate of dissolution of the container. This solid may
also be present in the contents of the container.
25 Dissolution of the solid in water is sufficient to cause an
acceleration in the break-up of the container, particularly
if a gas is generated, when the physical agitation caused
may, for example, result in the virtually immediate release
of the contents form the container.

30

Examples of such solids are alkali or alkaline earth metal, such as sodium, potassium, magnesium or calcium, bicarbonate or carbonate, in conjunction with an acid.

- 5 Suitable acids are, for example acidic substances having carboxylic or sulfonic acid groups or salts thereof. Examples are cinnamic, tartaric, mandelic, fumaric, maleic, malic, palmoic, citric and naphthalene disulfonic acids.
- 10 Any water-soluble polymer (which term is taken to include water-dispersible) may be used to form the compartments. Examples of water-soluble polymers are poly(vinyl alcohol) (PVOH), cellulose derivatives such as hydroxypropyl methyl cellulose (HPMC) and gelatin. An example of a preferred 15 PVOH is ethoxylated PVOH. The PVOH may be partially or fully alcoholised or hydrolysed. For example it may be from 40 to 100%, preferably from 70 to 92%, more preferably about 88% or about 92%, alcoholised or hydrolysed. The degree of hydrolysis is known to influence the temperature at which 20 the PVOH starts to dissolve in water. 88% hydrolysis corresponds to a film soluble in cold (ie room temperature) water, whereas 92% hydrolysis corresponds to a film soluble in warm water. A preferred PVOH which is already in a form suitable for injection moulding is sold in the form of 25 granules under the name CP1210T05 by Soltec Developpement SA of Paris, France.

- Thus by choosing an appropriate polymer it is possible to ensure that the walls of the container dissolve at a desired 30 temperature. Thus they may be cold water (20°C) soluble, but may be insoluble in cold water and only become soluble in

warm or hot water having a temperature of, for example, 30°C, 40°C, 50°C or even 60°C.

The container walls generally have a thickness such that the
5 container is rigid. For example, the outside walls and any
inside walls may independently have a thickness of greater
than 100µm, for example greater than 150µm or greater than
200µm, 300µm, 400µm, 500µm, 750µm or 1mm. Typically the
thicknesses are from 200µm to 1,500µm, preferably 300µm to
10 800µm. If different compartments having different wall
dissolution times are required, different wall thicknesses
for each compartment may be used. A thickness difference of
from 100µm to 500µm, preferably 250µm to 350µm, would give a
suitable difference in dissolution times.

15

The container may have any shape, but suitably is generally
cuboid. The top wall may be formed by the sealing film and
the side walls, inside walls and base wall may be formed by
the injection moulded part of the container, hereinafter
20 sometimes referred to as the receptacle part.

The receptacle part contains one or more compartments. For
example it can contain 2, 3, 4, 5 or 6 or more compartments.
At least one or two, and preferable all, of the compartments
25 have openings on the outside of the container. The openings
may independently be on any side of the container. Thus,
for example, all of the openings may be on one side of the
container. Alternatively, one side of the container may
have one or more openings and at least one other side of the
30 container may have one or more openings. For example, for a
container with two openings, the openings may both be on the

- same or different sides of the container. If they are on different sides, the sides may be, for example, adjacent to, spaced apart from or opposite each other, preferably the openings are spaced apart from or opposite each other. As a 5 further example, for a container with three openings, the openings may all be on one side of the container, the openings may all be on different sides of the container, or the container may have one opening on one side and two openings on another side. These openings may be, for 10 example, on adjacent, spaced apart or opposite sides of the container. As a yet further example, for a container with four openings, the openings may all be on one side of the container, the openings may all be on different sides of the container, or the container may have two openings on one 15 side and two openings on another side, or the container may have two openings on one side and one opening on each of two other sides. These openings may be, for example, on adjacent, spaced apart or opposite sides of the container.
- 20 Desirably, and especially when all of the openings are on one side of the container, the openings extend substantially across all of the face of the container except for that part of the face which is required as a surface for sealing the films to the container. Said part may be, for example, an 25 inward or outward flange. However, the openings may independently only extend across part of a surface of a container. For example they may extend over from 10 to 90% or 30 to 70% of the area of a side.
- 30 The dividing wall or walls of the container preferably terminate at the top of the receptacle part, i.e. in the same plane as the top edges of the side walls, such that

when the receptacle part is closed by the sealing part the contents of the compartments cannot mix.

The container may be formed with an opening, for example a depression, formed in a side wall or in the base wall, and preferably being open in the outward direction. That is to say, it does not form part of the main volume defined by the container. Preferably the opening is adapted to receive, in a press-fit manner, a solid block, for example a tablet or ball, of a composition useful in a washing process. The opening may also receive a non-compressed composition, for example a gel, which is allowed to set in the opening. A composition held in such an opening may be released before the contents of the container are released.

15

The polymer may be injection moulded at any suitable temperature. A suitable moulding temperature, especially for PVOH, is from 180°C to 220°C, depending upon the formulation selected and the melt flow required.

20

Each container may be individually moulded. It is also possible to mould the containers a conjoined line or a two dimensional array. The containers are then filled with the desired compositions. Before or after the filling step it is possible, if desired, to separate individual containers if more than one container has been moulded together.

Since the containers have more than one compartment, each compartment is filled with a composition. The compositions in each compartment may be the same or different. Each compartment may be filled simultaneously or at different

times. If all of the compartments have openings on the same side, the compartments may all be filled at the same time. However, if the compartments have openings on different sides, they may need to be filled at different times, with
5 the orientation of the container being changed in between the filling operations. It may also be necessary to seal the opening of the filled compartment before the orientation of the container is changed. For example, in order to fill a container, especially one in the form of a cuboid,
10 consisting of two compartments separated by an internal wall and having openings on opposite sides, the container is initially positioned with one opening upwards, the compartment with the uppermost opening is filled and the opening is then sealed with a first film. The container is
15 then turned upside down, and the operation repeated to fill the other compartment with a composition and then seal it with a second film.

At least one, and preferably all, of the films dissolve or
20 disperse to release the contents of the compartments which they seal before the walls of the container dissolve.

If all of the compartments have openings on the same side of the container one film or a plurality of films may be used
25 to seal the openings. However, if a single film is used to seal all the openings, or if the same film is used to seal all the openings at different times, at least part of the film must be treated or otherwise modified in order to ensure that at least two compartments are sealed with films
30 having different dissolution characteristics.

When at least two different films are used to seal different openings, the films may have different dissolution characteristics from each other at the time of sealing, or the characteristics may be modified after the compartments
5 have been sealed.

In order to ensure that films have different dissolution characteristics, the films may be chosen to dissolve at different temperatures. For example, the films may comprise
10 PVOH polymers having different degrees of hydrolysis. The films may also be chosen to dissolve at different pHs. It is also possible to ensure that the films take different times to dissolve to achieve a sequential release of compositions from different compartments, even when the external
15 environment of the containers has not changed. This may be achieved, for example, by using films which are of the same or different composition but which are of different thicknesses. It is also possible to treat one or more of the films after they have sealed the openings. For example, one
20 or more of the films may be covered by another film. If this is the same film it will simply retard dissolution of the film by increasing the effective thickness of the film layer. If is a different film, it may alter other dissolution properties. For example covering a cold water
25 soluble film with a warm water soluble film will ensure that the resultant composite film will only dissolve in warm water. Other mean for treating the film include increasing cross-linking by exposure to a cross-linking inducing chemical, such as boronic acid, or exposure to an
30 electromagnetic stimulus such as UV light. Another technique is to coat the film with a compound or composition which can repel or attract water. Compounds may be applied to the film

by any suitable technique, convenient techniques for applying thin layers of compound onto the film include techniques used in the printing industry, such as flexography, letterpress, gravure and silkscreen. Other 5 techniques include transfer coating, roller coating or otherwise spray coating.

If a single film is used, it is possible to treat at least part of the surface before or after it seals the openings of 10 the container. Any of the above treatments may be used, alone or in combination.

It is possible to use the same film for two compartments and then rely on one of the compositions in one of the 15 compartments to modify the film closing that compartment. Examples of such an affect can be achieved by the addition of plasticisers in the composition or cross-linking agents, such as boronic acid.

20 The films may be sealed to close the openings by any means. The two parts may be sealed, for example, by means of an adhesive. A suitable adhesive is water or a solution of PVOH. The adhesive can be applied to the sides of the openings or to the films by spraying, transfer coating, 25 roller coating or otherwise coating, or the films can be passed through a mist of the adhesive. The parts can also be made tacky such that they adhere to each other without the need for a separate adhesive. Thus they can be heated, such that they adhere to each other when they touch.

30

The container may also be wrapped in the film. If it is desired to have an attractive appearance with a smooth film,

- the film can be shrink-wrapped around the container. This can be done by pre-stretching the film, for example by biaxial orientation, and then heating it to shrink it around the container. The film may also be thermoformed around 5 part of the container by placing the container in a pocket of the film held in a thermoforming mould. An opening in the remaining part of the container can then be sealed with another film.
- 10 The parts may also be sealed by heat sealing or infra-red, radio frequency, ultrasonic, laser, solvent, vibration, electromagnetic, hot gas, hot plate, insert bonding friction sealing or by spin welding. Ultrasonic or laser sealing is preferably used. The seal desirably is water-soluble.
- 15 If heat sealing is used, a suitable sealing temperature is, for example, 120 to 195°C, for example 140 to 150°C. A suitable sealing pressure is, for example, from 250 to 600 kPa. Examples of sealing pressures are 276 to 552 kPa (40 20 to 80 p.s.i.), especially 345 to 483 kPa (50 to 70 p.s.i.) or 400 to 800 kPa (4 to 8 bar), especially 500 to 700 kPa (5 to 7 bar) depending on the heat sealing machine used. Suitable sealing dwell times are at least 0.4 seconds, for example 0.4 to 2.5 seconds.

25 The sealing films generally dissolve in water before the receptacle part of the container. The films therefore generally have thicknesses which are less than the wall thickness of the receptacle part. In general, at least one 30 of the films dissolves in water (at least to the extent of allowing the composition in the receptacle part to be partly

or completely dissolved by the water) at 40°C in less than 5 minutes, preferably less than 2 minute.

It is possible for one or more of the sealing films to have 5 incorporated therein a composition. Thus, for example, one or more of the films can themselves contain compositions formed in the films by a previous operation such as thermoforming or vertical form fill sealing.

10 The containers of the present invention contain two or more compositions, and can have a particularly attractive appearance since the compositions, which may be identical or different, are held in a fixed position in relation to each other. The compositions can be easily differentiated to 15 accentuate their difference. For example, the compositions can have a different physical appearance, or can be coloured differently.

Figure 1 of the accompanying drawings illustrates a 20 container which is split into two compartments. The container consists of a cuboid with solid faces 1 and two openings 2 on opposite sides of the member. Figure 2 illustrates a cross-section of the member of container 1 taken along the line II of Figure 1. One compartment can be 25 filled with a composition and the opening closed by a film. The container can then be turned upside down and the process repeated to fill and seal the other compartment with a film having different water dissolution characteristics. The composition(s) which can be held in each compartment of 30 the containers of the present invention may independently be a fabric care, surface care or dishwashing composition.

Thus, for example, they may be a dishwashing, water-softening, laundry or detergent composition, or a rinse aid. Such compositions may be suitable for use in a domestic washing machine. The compositions may also independently be
5 a disinfectant, antibacterial or antiseptic composition, or a refill composition for a trigger-type spray. Such compositions are generally packaged in total amounts of from 5 to 100 g, especially from 15 to 40 g. For example, a laundry composition may weigh from 15 to 40g, a dishwashing
10 composition may weigh from 15 to 30 g and a water-softening composition may weigh from 15 to 40 g.

If the composition is an aqueous liquid having a relatively high water content, for example above 5 wt% water, it may be
15 necessary to take steps to ensure that the liquid does not attack the water-soluble polymer if it is soluble in cold water, or water up to a temperature of, say, 35°C. Steps may be taken to treat the inside surfaces of the container, for example by coating it with agents such as PVdC
20 (poly(vinylidene dichloride)) or PTFE (polytetrafluoroethylene), or to adapt the composition to ensure it does not dissolve the polymer. For example, it has been found that ensuring the composition has a high ionic strength or contains an agent which minimises water
25 loss through the walls of the container will prevent the composition from dissolving the polymer from the inside. This is described in more detail in EP-A-518689 and WO 97/27743.
30 The compartments may be completely filled or only partially filled. Each composition independently may be a solid. For

example, it may be a particulate or granulated solid, or a tablet. Each composition may also independently be a liquid, which may be thickened or gelled if desired. The liquid composition may be non-aqueous or aqueous, for 5 example comprising less than or more than 5% or less than or more than 10wt% total or free water. Desirably the compositions contain less than 80 wt% water.

Each composition may have more than one phase. For example 10 each composition may comprise an aqueous composition and a liquid composition which is immiscible with the aqueous composition. Each composition may also comprise a liquid composition and a separate solid composition, for example in the form of a ball, pill or speckles.

15

Thus the composition within the container, or an individual compartment, need not be uniform. For example, during manufacture the container or compartment could first be fed with a settable composition, for example, a gel, and then 20 with a different composition. The first composition could dissolve slowly in the washing process so as to deliver its charge over a long period within the washing process. This might be useful, for example, to provide an immediate, delayed or sustained delivery of a component such as a 25 softening agent.

The compositions in each compartment may be the same or different. If they are different, they may, nevertheless, have one or more individual components in common.

30

The containers of the present invention may have any desired shape. For example the container can have a irregular or

regular geometrical shape such as a cube, cuboid, pyramid, dodecahedron or cylinder. The cylinder may have any desired cross-section, such as a circular, triangular or square cross-section.

5

The individual compartments in the container need not necessarily be regular or identical. For example, if the final container has a cuboid shape, the individual compartments may have different sizes to accommodate

10 different quantities of compositions.

The compartments may have the same or different size and/or shape. In general, if it is desired to have compartments containing different quantities of components, the

15 compartments have volume ratios of from 2:1 to 20:1, especially from 4:1 to 10:1.

The container may also have a hook portion so that it can be hung, for example, from an appropriate place inside a

20 dishwashing machine.

The containers produced by the process of the present invention may, if desired, have a maximum dimension of 5 cm, excluding any flanges. For example, a container may have a

25 length of 1 to 5 cm, especially 3.5 to 4.5 cm, a width of 1.5 to 3.5 cm, especially 2 to 3 cm, and a height of 1 to 2 cm, especially 1.25 to 1.75 cm.

If more than one composition is present, the compositions

30 may be appropriately chosen depending on the desired use of the article.

If the article is for use in laundry washing, the primary composition may comprise, for example, a detergent, and the secondary composition may comprise a bleach, stain remover, water-softener, enzyme or fabric conditioner. The article
5 is adapted to release the compositions at different times during the laundry wash. For example, a bleach or fabric conditioner is generally released at the end of a wash, and a water-softener is generally released at the start of a wash. An enzyme may be released at the start or the end of
10 a wash.

If the article is for use as a fabric conditioner, the primary composition may comprise a fabric conditioner and the secondary component may comprise an enzyme which is
15 released before or after the fabric conditioner in a rinse cycle.

If the article is for use in dish washing the primary composition may comprise a detergent and the secondary
20 composition may comprise a water-softener, salt, enzyme, rinse aid, bleach or bleach activator. The article is adapted to release the compositions at different times during the laundry wash. For example, a rinse aid, bleach or bleach activator is generally released at the end of a
25 wash, and a water-softener, salt or enzyme is generally released at the start of a wash. The article may also have more than two compartments adapted to release compositions at different times. For example a three compartment container may contain a bleach, a bleach activator and an
30 enzyme in different compartments. A four compartment container may also contain a salt in a fourth compartment.

Examples of surface care compositions are those used in the field of surface care, for example to clean, treat or polish a surface. Suitable surfaces are, for example, household surfaces such as worktops, as well as surfaces of sanitary 5 ware, such as sinks, basins and lavatories.

The ingredients of each composition depend on the use of the composition. Thus, for example, the composition may contain surface active agents such as an anionic, nonionic, 10 cationic, amphoteric or zwitterionic surface active agents or mixtures thereof.

Examples of anionic surfactants are straight-chained or branched alkyl sulfates and alkyl polyalkoxylated sulfates, 15 also known as alkyl ether sulfates. Such surfactants may be produced by the sulfation of higher C₈-C₂₀ fatty alcohols.

Examples of primary alkyl sulfate surfactants are those of formula:



wherein R is a linear C₈-C₂₀ hydrocarbyl group and M is a water-solubilising cation. Preferably R is C₁₀-C₁₆ alkyl, for example C₁₂-C₁₄, and M is alkali metal such as lithium, sodium or potassium.

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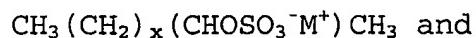
Examples of secondary alkyl sulfate surfactants are those which have the sulfate moiety on a "backbone" of the molecule, for example those of formula:



30 wherein m and n are independently 2 or more, the sum of m+n typically being 6 to 20, for example 9 to 15, and M is a

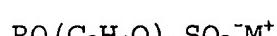
water-solubilising cation such as lithium, sodium or potassium.

Especially preferred secondary alkyl sulfates are the (2,3) 5 alkyl sulfate surfactants of formulae:



10 for the 2-sulfate and 3-sulfate, respectively. In these formulae x is at least 4, for example 6 to 20, preferably 10 to 16. M is cation, such as an alkali metal, for example lithium, sodium or potassium.

15 Examples of alkoxylated alkyl sulfates are ethoxylated alkyl sulfates of the formula:

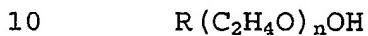


20 wherein R is a C₈-C₂₀ alkyl group, preferably C₁₀-C₁₈ such as a C₁₂-C₁₆, n is at least 1, for example from 1 to 20, preferably 1 to 15, especially 1 to 6, and M is a salt-forming cation such as lithium, sodium, potassium, ammonium, alkylammonium 25 or alkanolammonium. These compounds can provide especially desirable fabric cleaning performance benefits when used in combination with alkyl sulfates.

The alkyl sulfates and alkyl ether sulfates will generally 30 be used in the form of mixtures comprising varying alkyl chain lengths and, if present, varying degrees of alkoxylation.

Other anionic surfactants which may be employed are salts of fatty acids, for example C₈-C₁₈ fatty acids, especially the sodium or potassium salts, and alkyl, for example C₈-C₁₈, 5 benzene sulfonates.

Examples of nonionic surfactants are fatty acid alkoxylates, such as fatty acid ethoxylates, especially those of formula:



wherein R is a straight or branched C₈-C₁₆ alkyl group, preferably a C₉-C₁₅, for example C₁₀-C₁₄, alkyl group and n is at least 1, for example from 1 to 16, preferably 2 to 12, 15 more preferably 3 to 10.

The alkoxylated fatty alcohol nonionic surfactant will frequently have a hydrophilic-lipophilic balance (HLB) which ranges from 3 to 17, more preferably from 6 to 15, most 20 preferably from 10 to 15.

Examples of fatty alcohol ethoxylates are those made from alcohols of 12 to 15 carbon atoms and which contain about 7 moles of ethylene oxide. Such materials are commercially 25 marketed under the trademarks Neodol 25-7 and Neodol 23-6.5 by Shell Chemical Company. Other useful Neodols include Neodol 1-5, an ethoxylated fatty alcohol averaging 11 carbon atoms in its alkyl chain with about 5 moles of ethylene oxide; Neodol 23-9, an ethoxylated primary C₁₂-C₁₃ alcohol 30 having about 9 moles of ethylene oxide; and Neodol 91-10, an ethoxylated C₉-C₁₁ primary alcohol having about 10 moles of ethylene oxide.

Alcohol ethoxylates of this type have also been marketed by Shell Chemical Company under the Dobanol trademark. Dobanol 91-5 is an ethoxylated C₉-C₁₁ fatty alcohol with an average 5 of 5 moles ethylene oxide and Dobanol 25-7 is an ethoxylated C₁₂-C₁₅ fatty alcohol with an average of 7 moles of ethylene oxide per mole of fatty alcohol.

Other examples of suitable ethoxylated alcohol nonionic 10 surfactants include Tergitol 15-S-7 and Tergitol 15-S-9, both of which are linear secondary alcohol ethoxylates available from Union Carbide Corporation. Tergitol 15-S-7 is a mixed ethoxylated product of a C₁₁-C₁₅ linear secondary alkanol with 7 moles of ethylene oxide and Tergitol 15-S-9 15 is the same but with 9 moles of ethylene oxide.

Other suitable alcohol ethoxylated nonionic surfactants are Neodol 45-11, which is a similar ethylene oxide condensation products of a fatty alcohol having 14-15 carbon atoms and 20 the number of ethylene oxide groups per mole being about 11. Such products are also available from Shell Chemical Company.

Further nonionic surfactants are, for example, C₁₀-C₁₈ alkyl 25 polyglycosides, such as C₁₂-C₁₆ alkyl polyglycosides, especially the polyglucosides. These are especially useful when high foaming compositions are desired. Further surfactants are polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glyciamides and ethylene oxide-propylene 30 oxide block polymers of the Pluronic type.

Examples of cationic surfactants are those of the quaternary ammonium type.

The total content of surfactants in the composition is
5 desirably 60 to 95 wt%, especially 75 to 90 wt%. Desirably
an anionic surfactant is present in an amount of 50 to 75
wt%, the nonionic surfactant is present in an amount of 5 to
50 wt%, and/or the cationic surfactant is present in an
amount of from 0 to 20 wt%. The amounts are based on the
10 total solids content of the composition, i.e. excluding any
solvent which may be present.

The compositions, particularly when used as laundry washing
or dishwashing compositions, may also independently comprise
15 enzymes, such as protease, lipase, amylase, cellulase and
peroxidase enzymes. Such enzymes are commercially available
and sold, for example, under the registered trade marks
Esperase, Alcalase and Savinase by Nova Industries A/S and
Maxatase by International Biosynthetics, Inc. Desirably
20 the enzymes are independently present in the compositions in
an amount of from 0.5 to 3 wt%, especially 1 to 2 wt%, when
added as commercial preparations they are not pure and this
represents an equivalent amount of 0.005 to 0.5 wt% of pure
enzyme.

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The compositions may, if desired, independently comprise a
thickening agent or gelling agent. Suitable thickeners are
polyacrylate polymers such as those sold under the trade
mark CARBOPOL, or the trade mark ACUSOL by Rohm and Haas
30 Company. Other suitable thickeners are xanthan gums. The
thickener, if present, is generally present in an amount of
from 0.2 to 4 wt%, especially 0.5 to 2 wt%.

Compositions used in dishwashing independently usually comprise a detergency builder. The builders counteract the effects of calcium, or other ion, water hardness. Examples 5 of such materials are citrate, succinate, malonate, carboxymethyl succinate, carboxylate, polycarboxylate and polyacetyl carboxylate salts, for example with alkali metal or alkaline earth metal cations, or the corresponding free acids. Specific examples are sodium, potassium and lithium 10 salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, C₁₀-C₂₂ fatty acids and citric acid. Other examples are organic phosphonate type sequestering agents such as those sold by Monsanto under the trade mark Dequest and alkylhydroxy phosphonates. Citrate salts and 15 C₁₂-C₁₈ fatty acid soaps are preferred. Further builders are; phosphates such as sodium, potassium or ammonium salts of mono-, di- or tri-poly or oligo-phosphates; zeolites; silicates, amorphous or structured, such as sodium, potassium or ammonium salts.

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Other suitable builders are polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic and copolymers and their salts, such 25 as those sold by BASF under the trade mark Sokalan.

The builder is desirably present in an amount of up to 90 wt%, preferably 15 to 90 wt%, more preferable 15 to 75 wt%, relative to the total weight of the composition. Further details of suitable components are given in, for example, 30 EP-A-694,059, EP-A-518,720 and WO 99/06522.

The compositions can also optionally comprise one or more additional ingredients. These include conventional detergent composition components such as further surfactants, bleaches, bleach enhancing agents, builders, 5 suds boosters or suds suppressors, anti-tarnish and anti-corrosion agents, organic solvents, co-solvents, phase stabilisers, emulsifying agents, preservatives, soil suspending agents, soil release agents, germicides, pH adjusting agents or buffers, non-builder alkalinity sources, 10 chelating agents, clays such as smectite clays, enzyme stabilizers, anti-limescale agents, colourants, dyes, hydrotropes, dye transfer inhibiting agents, brighteners, and perfumes. If used, such optional ingredients will generally constitute no more than 10 wt%, for example from 1 15 to 6 wt%, the total weight of the compositions.

- Compositions which comprise an enzyme may optionally contain materials which maintain the stability of the enzyme. Such enzyme stabilizers include, for example, polyols such as 20 propylene glycol, boric acid and borax. Combinations of these enzyme stabilizers may also be employed. If utilized, the enzyme stabilizers generally constitute from 0.1 to 1 wt% of the compositions.
- 25 The compositions may optionally comprise materials which serve as phase stabilizers and/or co-solvents. Examples are C₁-C₃ alcohols such as methanol, ethanol and propanol. C₁-C₃ alkanolamines such as mono-, di- and triethanolamines can also be used, by themselves or in combination with the 30 alcohols. The phase stabilizers and/or co-solvents can, for example, constitute 0 to 1 wt%, preferably 0.1 to 0.5 wt%, of the composition.

The compositions may optionally comprise components which adjust or maintain the pH of the compositions at optimum levels. The pH may be from, for example, 1 to 13, such as 8 to 11 depending on the nature of the composition. For example a dishwashing composition desirably has a pH of 8 to 11, a laundry composition desirable has a pH of 7 to 9, and a water-softening composition desirably has a pH of 7 to 9. Examples of pH adjusting agents are NaOH and citric acid.

10

The above examples may be used for dish or fabric washing. In particular dish washing formulations are preferred which are adapted to be used in automatic dish washing machines. Due to their specific requirements specialised formulation 15 is required and these are illustrated below

Amounts of the ingredients can vary within wide ranges, however preferred automatic dishwashing detergent compositions herein (which typically have a 1% aqueous solution pH of above 8, more preferably from 9.5 to 12, most preferably from 9.5 to 10.5) are those wherein there is present: from 5% to 90%, preferably from 5% to 75%, of builder; from 0.1% to 40%, preferably from 0.5% to 30%, of bleaching agent; from 0.1% to 15%, preferably from 0.2% to 10%, of the surfactant system; from 0.0001% to 1%, preferably from 0.001% to 0.05%, of a metal-containing bleach catalyst; and from 0.1% to 40%, preferably from 0.1% to 20% of a water-soluble silicate. Such fully-formulated embodiments typically further comprise from 0.1% to 15% of a polymeric dispersant, from 0.01% to 10% of a chelant, and from 0.00001% to 10% of a deterotive enzyme, though further additional or adjunct ingredients may be present. Detergent

compositions herein in granular form typically limit water content, for example to less than 7% free water, for better storage stability.

- 5 Non-ionic surfactants useful in ADW (Automatic Dish Washing) compositions of the present invention desirably include surfactant(s) at levels of from 2% to 60% of the composition. In general, bleach-stable surfactants are preferred. Non-ionic surfactants generally are well known,
10 being described in more detail in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detergent Systems", incorporated by reference herein.
- 15 Preferably the ADW composition comprises at least one non-ionic surfactant. One class of non-ionics are ethoxylated non-ionic surfactants prepared by the reaction of a monohydroxy alkanol or alkylphenol with 6 to 20 carbon atoms with preferably at least 12 moles particularly preferred at
20 least 16 moles, and still more preferred at least 20 moles of ethylene oxide per mole of alcohol or alkylphenol.

Particularly preferred non-ionic surfactants are the non-ionic from a linear chain fatty alcohol with 16-20 carbon atoms and at least 12 moles particularly preferred at least 16 and still more preferred at least 20 moles of ethylene oxide per mole of alcohol.

According to one preferred embodiment the non-ionic surfactant additionally comprise propylene oxide units in the molecule. Preferably this PO units constitute up to 25% by weight, preferably up to 20% by weight and still more

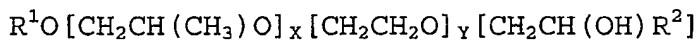
preferably up to 15% by weight of the overall molecular weight of the non-ionic surfactant. Particularly preferred surfactants are ethoxylated mono-hydroxy alkanols or alkylphenols, which additionally comprises polyoxyethylene-
5 polyoxypropylene block copolymer units. The alcohol or alkylphenol portion of such surfactants constitutes more than 30%, preferably more than 50%, more preferably more than 70% by weight of the overall molecular weight of the non-ionic surfactant.

10

Another class of non-ionic surfactants includes reverse block copolymers of polyoxyethylene and polyoxypropylene and block copolymers of polyoxyethylene and polyoxypropylene initiated with trimethylolpropane.

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Another preferred non-ionic surfactant can be described by the formula:

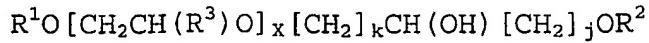


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wherein R^1 represents a linear or branched chain aliphatic hydrocarbon group with 4-18 carbon atoms or mixtures thereof, R^2 represents a linear or branched chain aliphatic hydrocarbon rest with 2-26 carbon atoms or mixtures thereof, x is a value between 0.5 and 1.5 and y is a value of at least 15.

Another group of preferred nonionic surfactants are the end-capped polyoxyalkylated non-ionics of formula:

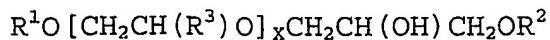
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wherein R¹ and R² represent linear or branched chain, saturated or unsaturated, aliphatic or aromatic hydrocarbon groups with 1-30 carbon atoms, R³ represents a hydrogen atom or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl or 2-methyl-2-butyl group , x is a value between 1 and 30 and, k and j are values between 1 and 12, preferably between 1 and 5. When the value of x is ≥ 2 each R³ in the formula above can be different. R¹ and R² are preferably linear or branched chain, saturated or unsaturated, 10 aliphatic or aromatic hydrocarbon groups with 6-22 carbon atoms, where group with 8 to 18 carbon atoms are particularly preferred. For the group R³ H, methyl or ethyl are particularly preferred. Particularly preferred values for x are comprised between 1 and 20, preferably between 6 15 and 15.

As described above, in case x ≥ 2 , each R³ in the formula can be different. For instance, when x=3, the group R³ could be chosen to build ethylene oxide (R³=H) or propylene oxide 20 (R³=methyl) units which can be used in every single order for instance (PO) (EO) (EO), (EO) (PO) (EO), (EO) (EO) (PO), (EO) (EO) (EO), (PO) (EO) (PO), (PO) (PO) (EO) and (PO) (PO) (PO). The value 3 for x is only an example and bigger values can be chosen whereby a higher number of variations of (EO) or 25 (PO) units would arise.

Particularly preferred end-capped polyoxyalkylated alcohols of the above formula are those where k=1 and j=1 originating molecules of simplified formula:



The use of mixtures of different non-ionic surfactants is particularly preferred in ADW formulations for example mixtures of alkoxylated alcohols and hydroxy group containing alkoxylated alcohols.

5

The containers may themselves be packaged in outer containers if desired, for example non-water soluble containers which are removed before the water-soluble containers are used.

10

In use the container are simply added to water where they dissolve. Thus they may be added in the usual way to a dishwasher or laundry machine, especially in the dishwashing compartment or a drum. They may also be added to a quantity
15 of water, for example in a bucket or trigger-type spray.

)

CLAIMS

1. A water-soluble, injection-moulded container comprising at least one compartment and having a first opening closed by a first film and a second opening closed by a second film, wherein the first film and the second film have different water dissolution characteristics.
2. A water-soluble, injection-moulded container comprising at least two compartments, a first compartment containing a first composition and having a first opening closed by a first film and a second compartment containing a second composition and having a second opening closed by a second film, wherein the first film and the second film have different water dissolution characteristics.
3. A container according to claim 1 or 2 with the proviso that the container does not comprise a member having at least two openings positioned on different sides of the member, wherein each opening is closed by a film having different water dissolution characteristics.
4. A container according to any one of the preceding claims wherein the first film and the second film dissolve in water before the injection-moulded walls of the container.
5. A container according to any one of claims 1 to 4 wherein the first opening and the second opening are on different sides of the container.

6. A container according to any one of claims 1 to 4 wherein the first opening and the second opening are on the same side of the container.

5 7. A container according to any one of the preceding claims wherein the container walls comprise a poly(vinyl alcohol).

8. A container according to any one of the preceding 10 claims wherein at least one of the first film and the second film comprises a poly(vinyl alcohol).

9. A container according to any one of the preceding 15 claims wherein the first film and the second film start to dissolve in water having different temperatures.

10. A container according to any one of the preceding claims wherein the first film and the second film start to dissolve in water having different pHs.

20

11. A container according to any one of the preceding claims wherein the first film and the second film comprise different base polymers.

25 12. A container according to any one of claims 1 to 9 wherein the first film and the second film comprise poly(vinyl alcohol)s having different degrees of hydrolysis.

13. A container according to any one of claims 1 to 9 30 wherein the first film and the second film have different thicknesses.

14. A container according to any one of claims 1 to 9 wherein at least one of the first film and the second film comprises a coating to modify its dissolution characteristics.

5

15. A container according to any one of the preceding claims wherein the first film and the second film are sealed to the container by laser or ultrasonic sealing.

10 16. A container according to any one of claims 1 to 14 wherein the first film and/or the second film is thermoformed around the container.

15 17. A container according to any one of claims 1 to 14 wherein the first film and/or the second film is wrapped around the container.

20 18. A container according to any one of the preceding claims wherein the first film and the second film are different films.

25 19. A container according to any one of claims 1 to 17 wherein the first film and the second film are in the form of a single film in which different parts have different water dissolution characteristics.

30 20. A container according to any one of the preceding claims wherein the first compartment and the second compartment each contains a fabric care, surface care or dishwashing composition.

21. A container according to claim 20 wherein each composition is a dishwashing, water-softening, laundry, detergent or rinse aid composition.

5 22. A container according to any one of claims 1 to 20 which encases a disinfectant, antibacterial or antiseptic composition.

10 23. A container according to any one of the preceding claims which encases a refill composition for a trigger-type spray.

15 24. A process for preparing a container as defined in any one of the preceding claims which comprises forming the container comprising at least two compartments by injection-moulding, filling each compartment a composition and sealing each compartment with a film, wherein at least two sealing films have different water dissolution characteristics.

20 25. A process according to claim 24 wherein the two sealing films have different water dissolution characteristics at the time they seal each compartment.

25 26. A process according to claim 24 wherein the two sealing films have the same water dissolution characteristics at the time they seal each compartment and the water dissolution characteristic of at least one film is subsequently modified.

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/GB 02/02317

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B65D65/46 A61K9/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B65D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 823 816 A (WHEELER L ET AL) 16 July 1974 (1974-07-16) the whole document	1
Y	---	2-8, 13-25
Y	US 5 125 534 A (ROSE BARRY L ET AL) 30 June 1992 (1992-06-30) column 6, line 64 -column 8, line 61	2-8, 13-25
A	DE 199 41 480 A (HENKEL KGAA) 8 March 2001 (2001-03-08) the whole document	1-23
A	GB 2 241 485 A (NAT RES DEV) 4 September 1991 (1991-09-04) page 4, line 8 -page 8, line 9	1-23

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:

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- *&* document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 02/02317

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 3823816	A	16-07-1974	AR AU AU BE CA DE ES FR GB IT JP JP JP ZA	196325 A1 463254 B 5171973 A 794951 A1 990238 A1 2305280 A1 411206 A1 2170751 A5 1377452 A 977185 B 1043060 C 48082025 A 55032381 B 7300766 A		18-12-1973 17-07-1975 08-08-1974 29-05-1973 01-06-1976 09-08-1973 01-04-1976 14-09-1973 18-12-1974 10-09-1974 23-04-1981 02-11-1973 25-08-1980 25-09-1974
US 5125534	A	30-06-1992	NONE			
DE 19941480	A	08-03-2001	DE	19941480 A1		08-03-2001
GB 2241485	A	04-09-1991	AT AU AU CA DE DE DK EP EP ES FI WO GR HU HU IE JP KR NO NZ PT RU US ZA	178790 T 646244 B2 7443891 A 2077342 A1 69131129 D1 69131129 T2 517771 T3 0517771 A1 0878190 A1 2130136 T3 923924 A 9112795 A1 3030007 T3 62464 A2 218675 B 910693 A1 3247693 B2 177178 B1 923397 A 237290 A 96921 A ,B 2094044 C1 5474784 A 9101526 A		15-04-1999 17-02-1994 18-09-1991 03-09-1991 20-05-1999 14-10-1999 25-10-1999 16-12-1992 18-11-1998 01-07-1999 01-09-1992 05-09-1991 30-07-1999 28-05-1993 28-10-2000 11-09-1991 21-01-2002 20-03-1999 31-08-1992 25-11-1994 31-03-1993 27-10-1997 12-12-1995 25-11-1992